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**ELECTROCHEMICAL CONCENTRATION AND PURIFICATION OF
SPENT SODIUM BICARBONATE BLASTING MEDIA**

by

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13. ABSTRACT (Maximum 200 words)

The feasibility and economics of recovering the spent blast media generated in sodium bicarbonate depainting operations has been investigated. In laboratory-scale tests, a saturated sodium bicarbonate solution was converted to sodium hydroxide in an electrochemical cell containing a Nafion cation exchange membrane. Energy consumption was 2 kWh per pound of sodium bicarbonate treated and could be reduced by a factor of two by operating the cell at higher flow rates.

The proposed treatment train will essentially eliminate the need for off-site waste disposal, reducing the quantity of solid hazardous waste by over 99 percent and completely eliminating all liquid hazardous wastes. The capital costs of an electrochemical treatment system was estimated to be \$19,400 for a plant sized to treat 25 lb/day blast media. Estimated operating costs amount to \$2,270/yr, some 90 percent less than the \$26,850/yr needed for makeup of the blast media and off-site waste disposal when treatment is not used. The savings of \$24,580/yr correspond to a very short payback period of 0.8 years (9.5 months) for the capital cost.

It was concluded that by conserving resources and eliminating off-site waste disposal, treating the spent blast media has the potential for significantly reducing the overall costs for depainting.

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EXECUTIVE SUMMARY

The use of sodium bicarbonate blast media for paint stripping and degreasing meets one of the prime objectives of the Department of Defense's pollution prevention initiatives, namely the substitution of a process that uses environmentally benign chemicals for one that uses toxic organic solvents and/or chemicals. However, the process produces a relatively large amount of contaminated waste. The bulk of this waste consists of spent blast media, and its off-site disposal is not only costly in environmental terms, but is also a waste of a valuable resource. In this report, the feasibility of eliminating the waste disposal problem and recovering the spent blast media for reuse is investigated.

Electrochemical concentration and purification of spent sodium bicarbonate blasting media reduces the volume of toxic waste requiring disposal and at the same time reduces process costs by recovering the blasting medium and substantially reducing the cost of waste disposal. The process studied is based on treating the spent blast media in an electrochemical cell fitted with a cation exchange membrane for controlling ion transport. The cell is similar to those used in the chlor-alkali industry, but with the chloride-chlorine couple replaced with the more benign bicarbonate-carbon dioxide system. Electrochemical processing of the sodium bicarbonate produces a pure sodium hydroxide solution and a depleted bicarbonate effluent containing about 1000 ppm sodium which can be discharged to drain or reused for blasting or dust control. The sodium hydroxide may be sold as a byproduct, or converted back to sodium bicarbonate for reuse as the blasting medium by reaction with the carbon dioxide which is evolved in the electrochemical cell.

The objective of this program was to determine the feasibility of the electrochemical step, and to establish design and cost parameters for the treatment process. The electrochemical process was investigated in a laboratory-scale unit and a preliminary economic analysis, based on a conceptual design that included pretreatment steps for removing dissolved metals and suspended contaminants, was completed.

The experimental investigation confirmed that sodium bicarbonate can be converted to sodium hydroxide in an electrochemical membrane cell. Attempts to use gold, aluminum, and uncoated titanium as anode materials failed, but excellent results were obtained with platinum. Platinum-on-titanium electrodes, readily available commercially, are therefore recommended as anodes, and stainless steel can be used for the cathode. Du Pont Nafion 300 series cation exchange membranes performed successfully although, due to time limitations brought about by problems with the experimental equipment, sodium hydroxide concentrations achieved were limited to about 7 percent. However, the membranes tested can produce up to 20 percent sodium hydroxide and, if desired, the 900 series membranes which can produce 30 percent sodium hydroxide can be used.

In the laboratory tests, the electrochemical treatment was accomplished at a current efficiency of 75 percent and an energy input of 2 kWh per pound of sodium bicarbonate

treated. At a cost of 10¢/kWh, the power cost amounts to 20¢/lb, about one-third the cost of sodium bicarbonate blast media at 68¢/lb. Based on the performance characteristics of the experimental cell and data reported in the literature, it appears that energy costs can be reduced to about 10¢/lb by operating the cell at a higher electrolyte velocity than was used in the tests.

An economic analysis was completed for a treatment train designed for a small depainting shop using 25 lb/day of bicarbonate blast media. A previous study had shown that such an operation would generate about 37 lb/day of solid waste and 71 lb/day of liquid waste that require off site disposal. The reported costs for waste disposal and the supply of makeup blast media were used here for assessing the viability of the treatment option.

Treatment will essentially eliminate the need for off-site waste disposal, reducing the quantity of solid hazardous wastes by over 99 percent and completely eliminating all liquid hazardous wastes; less than 0.1 bbl/yr of hazardous waste will be generated by the treatment train. Electrochemical treatment will recover 95 percent of the spent sodium bicarbonate blast media for reuse; the other 5 percent can be discharged down the sewer as a non-hazardous waste. Pretreatment includes a reduction step in which ferrous sulfate is added to convert any hexavalent chromium present to the trivalent form. At the high pH of the sodium bicarbonate solution ($\text{pH} = 8.3$), the solubility of the metals of concern (chromium, lead and zinc) are well below their discharge limits. The metal precipitates and other suspended solids are removed by settling and cartridge filtration. If necessary, a belt skimmer can be added to remove oil and grease. Contaminant removal by pretreatment was not tested in this program, but is not expected to be a problem.

The cost of the electrochemical cell and power supply needed to treat the spent bicarbonate blast media is estimated to be about \$14,600, and another \$4,800 is required for the pretreatment equipment, for a total of \$19,400. The operating costs are about \$1,300/yr and \$2,270/yr including maintenance. This is some 90 percent less than the \$26,850/yr needed for makeup of the blast media and off-site waste disposal that is incurred when the spent blast media is not treated. Electrochemical treatment represents a savings of \$24,580/yr and corresponds to a very short payback period of 0.8 yrs (9.5 months) for the capital cost of the 25 lb/day spent blast media treatment train.

An economic analysis was also carried out for a larger plant size, a longer daily operation time, and varying unit costs of waste disposal. Except for very low unit waste disposal costs, representative of non-hazardous waste disposal, the period to payback the capital costs of the treatment train ranged from a little more than one year to about three months. After the payback period, electrochemical treatment of the spent blast media will result in substantial savings in the annual operating costs ranging from \$5,000 to \$37,000 for a blast media flow of 25 lb/day and from \$30,000 to \$220,000 for a flow of 150 lb/day; the lower savings corresponds to non-hazardous waste disposal and the higher savings corresponds to high unit waste disposal costs representative of hazardous waste disposal.

In making the cost estimates, it was assumed that the automated electrochemical plant can be operated without additional labor costs. The labor associated with disposal of the hazardous wastes for untreated spent blast media will be offset by the labor associated with the operation of the electrochemical treatment train. Installation costs were not accounted for but are not expected to be significant as the electrochemical components are supplied in a skid-mounted assembly.

The success of the process depends on the ability to remove the heavy metal contaminants as well as the oil and grease from the spent blast media waste stream. The presence of these substances can lead to rapid membrane fouling and failure of the electrochemical system. Contaminant removal and membrane fouling was not tested in the present program, but will be investigated in detail in a Phase II pilot-scale program.

The preliminary economic analysis indicates that electrochemical treatment is potentially a cost effective means of eliminating the waste disposal problem associated with bicarbonate depainting. Furthermore, suitable electrochemical cells are widely available commercially, can be operated automatically, and their incorporation into a depainting shop is not expected to cause difficulties.

Before proceeding, however, it is recommended that the long-term performance of the process be assessed using a commercial electrochemical cell running on spent blast media obtained from a depainting operation. In addition to determining the effectiveness of the pretreatment, performance characteristics should be obtained for a range of concentrations of the depleted bicarbonate and the sodium hydroxide streams produced in the electrochemical cell. The data generated will allow a more detailed economic analysis to be completed and, if needed, allow more sophisticated pretreatments to be selected to prevent membrane fouling.

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1. OBJECTIVES

1.1 Introduction

In accordance with the Clean Air Act, organic solvents such as methylene chloride that have been widely used for paint stripping and degreasing are being phased out. In the aircraft industry in particular, solvent stripping generates large quantities of hazardous wastes. For example, it is estimated that nearly 500 gallons of chemicals along with 200,000 gallons of water are used for stripping a single aircraft, and that the effluents contain a further 1024 pounds of hazardous solids (1). Other, environmentally benign means of paint stripping are therefore being actively evaluated.

One alternative process that is being considered by the Department of Defense and other organizations is sodium bicarbonate blasting. In this process, sodium bicarbonate blast media and a water stream are blasted under pressures against the work piece (2, 3). An advantage over some other processes that are being considered is that minimal surface treatment is required because the sodium bicarbonate blast media removes oil and greases as well as the paint. In addition, the blast media is water soluble, making it easier to separate insoluble hazardous material, it is non-toxic, and it does not pose a fire or explosion hazard.

However, the spent bicarbonate blast media contains about 2 percent by volume of contaminants consisting of heavy metal particulates as well as oils and greases (2, 4). The concentration of these contaminants is sufficient to exceed local discharge limits to publicly owned treatment works (POTWs) and the entire spent blast media stream has to be collected in drums and disposed of off site (2). The U.S. Navy is currently disposing of the spent blast media stream as a hazardous waste. Because of increasing costs, environmental restrictions, and the legal complexity of waste disposal, means of reducing or eliminating the waste streams are essential to the economic viability of sodium bicarbonate blasting.

One means of removing the contaminants is to dissolve the bicarbonate in water to form a near-saturated solution and then to use conventional waste water treatment technologies to remove suspended solids and oil and grease. Recovery of the spent blast media from the purified solution then becomes an attractive option. However, simple evaporation to recover sodium bicarbonate crystals is not viable as the small amount of dissolved contaminants remaining in solution could accumulate in the system. These impurities, including for example the reagents used for flow enhancement of the dry blast media, could interfere with the sodium bicarbonate crystallization process.

Electrochemical treatment of the spent sodium bicarbonate is an attractive alternative means of recovering the blasting media. In this process, the bicarbonate solution is converted to sodium hydroxide in an electrochemical cell. This intermediate product can then be recarbonated with byproduct carbon dioxide and evaporated to recover dry sodium bicarbonate. The electrochemical step effectively purifies and concentrates the bicarbonate

solution.

1.2 Program Objectives

The overall objective of this investigation was to evaluate the technical feasibility of concentrating and purifying spent blast media from sodium bicarbonate blasting by electrochemical means, as well as its viability in terms of process economics and waste reduction. Specific objectives for the program were to determine:

- The performance of a laboratory-scale electrochemical cell in the batch mode
- The design and cost parameters needed to scale-up the process from a laboratory size unit to a pilot size unit

The upstream pretreatments of oil, grease and heavy metal removal, as well as the downstream production of sodium bicarbonate crystals, are relatively well established, and will be evaluated in a later program.

Experiments were run on a laboratory-scale electrochemical cell to determine performance factors such as:

- Maximum concentration of the sodium hydroxide stream
- Minimum concentration of the depleted bicarbonate effluent
- Current efficiency and electrical costs for the process
- Throughput rate and the estimated capital cost of the electrochemical cell

1.3 Scope

This report is written in 7 sections and one Appendix:

- Section 1 - Objectives. The problem of spent blast media treatment and the objectives of the test program are discussed.
- Section 2 - Background. The sodium bicarbonate blast media and electrochemical treatment processes are described in detail.
- Section 3 - Experimental Investigation. A description of the electrochemical cell and experimental flow system and the procedures for carrying out the test program are detailed.

- Section 4 - Results and Discussion. The results of the test program are presented and discussed in some detail.
- Section 5 - Cost Analysis. The capital and operating costs of a full-scale electrochemical treatment system are estimated and compared to the present method of no treatment.
- Section 6 - Conclusions.
- Section 7 - References.
- Appendix - Experimental Data. The raw test data are tabulated.

1.4 Acknowledgements

The authors gratefully acknowledge the assistance of Mr. Joseph Burke and Mr. Robert Tse in fabricating the test cell and setting up the power supply.

2. BACKGROUND

2.1 Sodium Bicarbonate Blasting

The sodium bicarbonate blast media used in depainting has a particle size of from 75 μm (for delicate substrates) up to 275 μm (for aircraft skin and airframe) (2). In the blasting process, the blast media is placed in a pressure pot and delivered by compressed air to a nozzle where it mixes with a water stream that is directed against the work surface. The water serves to dissipate the heat generated in the abrasive process and also reduces the amount of dust that escapes into the air. The amount of water used is typically about three times that of the amount of dry blast media, or about one-third of the amount needed to completely dissolve the blast media.

The spent blast media is collected as a wet slurry that may be separated under gravity into a solid and a liquid waste stream. Both these streams contain metal contaminants as well as oil and grease. Some data on the amount of these impurities, together with limits on their concentrations for discharge to local POTWs, are listed in Table 1 (2). As can be seen, the waste streams contain excessive quantities of some heavy metals and have to be disposed of off site. It is expected that costs for such disposal will continue to rise in the future, and there is the further disadvantage that even if properly disposed of, the wastes could remain the responsibility of the generator.

Another disadvantage of disposing the wastes is that the sodium value is lost. Because the sodium bicarbonate structure is destroyed in the blasting process, it would have to be dissolved and recrystallized if it is to be re-used. Once in solution, however, the insoluble contaminants can be removed by settling and flotation (4) or by filtration. It is seen in Figure 1 that two of the heavy metals of concern, namely lead and zinc, will be well below their local discharge limits of 1.5 and 6 mg/L at the high pH and carbonate concentration of the saturated bicarbonate solution. Although hexavalent chromium remains soluble in bicarbonate solutions, it may be sufficient to reduce it with an iron salt and co-precipitate it as trivalent chromium (5).

2.2 Electrochemical Processing

After the suspended contaminants are removed, the saturated sodium bicarbonate solution can be processed in an electrochemical cell to produce pure sodium hydroxide and a depleted bicarbonate waste stream suitable for disposal to drain. The overall reaction for the electrochemical process, which is shown schematically in Figure 2, is given by:



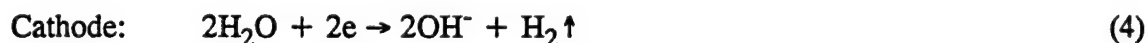
Table 1. Contaminants in Spent Blast Media Waste Streams (2)

Parameter	Solid Waste* (mg/kg)	Liquid Waste† (mg/L)	Local Discharge Limit (mg/L)
pH (units)	-	8.4	6-10
Oil and grease	-	49.1	200
TSS	-	253	365
Cadmium	2.72	0.033	0.2
Chromium	146.1	8.090	5.0
Copper	32.97	1.24	2.0
Lead	70.87	1.43	1.5
Manganese	2.77	0.022	3.0
Nickel	0.72	0.005	3.0
Zinc	281.33	5.99	6.0
Total Concent	533.5	318.9	-
* Total of solid plus leachable metals. † Total of suspended and dissolved metals.			

As seen, a carbon dioxide stream is also produced and may be used to convert the sodium hydroxide back to pure sodium bicarbonate:



The electrochemical cell shown in Figure 2 consists essentially of an anode, or positive electrode, and a cathode, or negative electrode, which are separated by a cation exchange membrane. The spent blast media solution is fed to the anode side of the membrane and the sodium hydroxide recovered from the cathode side. A dc voltage is applied across the cell to effect electrolysis of the water at the electrodes:



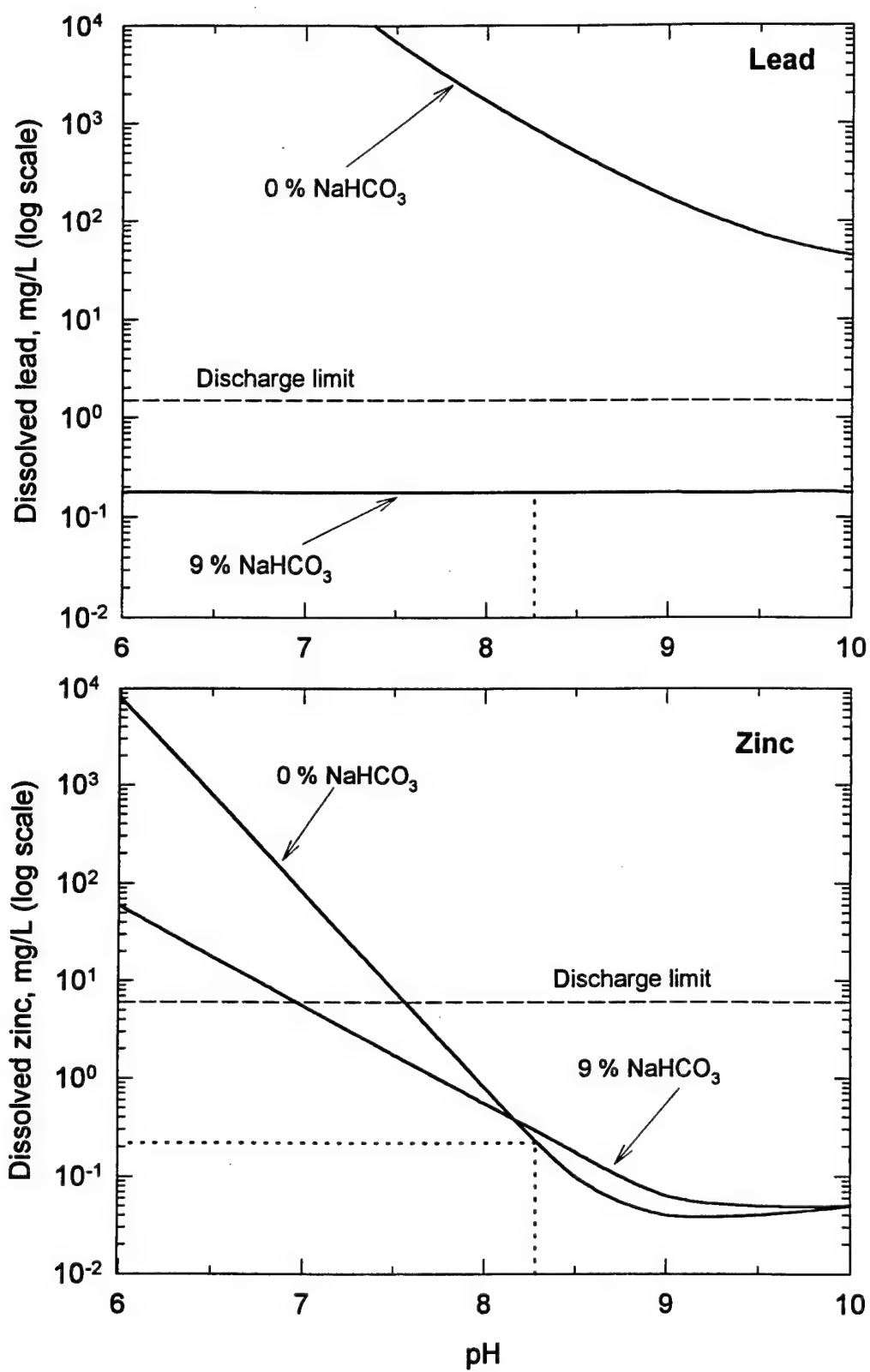
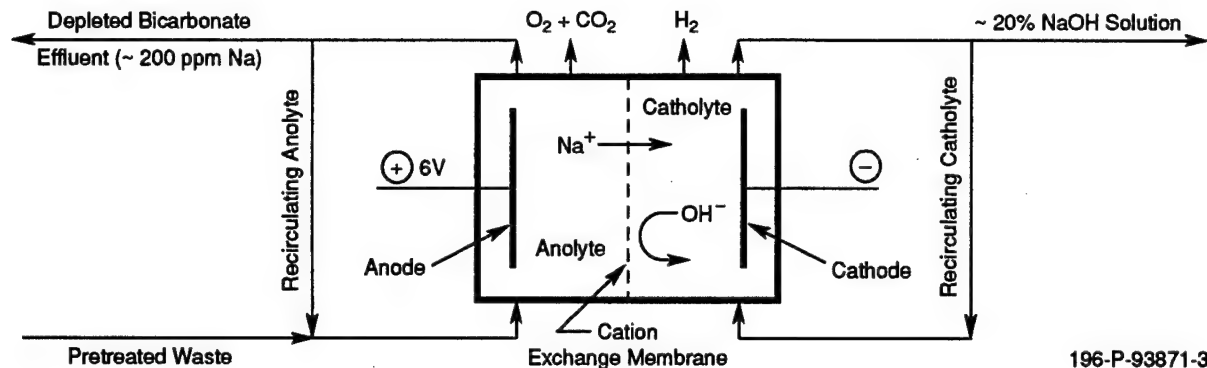


Figure 1. Solubility of Lead and Zinc in the Sodium Bicarbonate Solution (pH = 8.3)

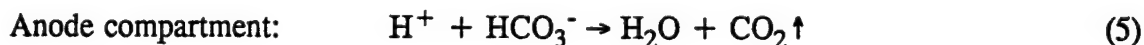


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Figure 2. Schematic Representation of the Electrochemical Process

The electric field also causes positive ions in the solution to migrate toward the cathode and negative ions to migrate toward the anode. The membrane is used to control the migration of these ions. As shown in Figure 2, the cation exchange membrane allows only positive ions to pass, resulting in an accumulation of sodium ions in the cathode region together with the hydroxyl ions produced at the cathode (Equation 4). Depending on the grade of membrane used, sodium hydroxide concentrations in the catholyte can reach from 15 to 35 percent (6).

The hydrogen ions produced at the anode also migrate toward the cathode, but before being transported through the membrane they react with the bicarbonate ions in the anode region with evolution of carbon dioxide:



The concentration of the sodium bicarbonate in the anolyte can be reduced to 200 ppm as sodium (7), so the effluent from the anode compartment may be discharged directly to drain.

Recently there have been significant advances in the technology of electrochemical processing for pollution control (8) and for resource recovery and synthesis (9). These advances make this a feasible technology for concentrating, purifying, and upgrading the sodium bicarbonate. In fact, the basis of the process described here has already been demonstrated at the pilot plant level for recovery of caustic soda from caustic effluents at textile mills (7).

It is noted that a 20 percent sodium hydroxide solution as may be produced in the cell contains 11.5 percent sodium, whereas the sodium content of the 9 percent (saturated) sodium bicarbonate feed solution is only 2.5 percent. This means that in addition to purifying the spent blast media, the electrochemical step effectively reduces the water content

by a factor of five. This concentrating effect reduces the cost of thermal evaporation to recover sodium bicarbonate crystals.

Another advantage of electrochemical processing is its simplicity and inherent flexibility. The operation of electrochemical cells can be automated and the availability of modern titanium/metal oxide anodes and high performance membranes with life expectancies of several years have resulted in considerably reduced maintenance requirements (9). Producing sodium hydroxide as an intermediate provides options of selling this valuable commodity, reusing some or all of it in the paint stripping operations, or converting it back to the bicarbonate as described above.

Although the basic electrochemical process has been demonstrated at the pilot level for a textile waste (7), the present investigation was undertaken to resolve questions regarding the potential for membrane and electrode fouling with the spent blast media stream, as well as to determine the optimum final concentrations of the anolyte and catholyte solutions. The Phase I "proof of concept" study is described in Section 3.

3. EXPERIMENTAL INVESTIGATION

The electrochemical tests were done using the bench-scale cell shown in Figure 3. It consists essentially of a cation exchange membrane and two gaskets sandwiched between two gold plated aluminum plates. The gaskets formed the anode and cathode compartments which were filled with a turbulence promoter (plastic mesh) that served to support the membrane and also to enhance mass transfer rates. The exposed metal within the gasket cutout formed the electrodes. These were connected to a 25 amp DC bridge power supply with a Variac®, capable of providing 115 V at up to 25 amps. Further specifications of the experimental equipment are summarized in Table 2.

Table 2. Specifications for the Electrochemical Cell

Component	Specification
Anode	Gold plated aluminum: 5 cm x 15 cm; area = 75 cm ² Platinum: 5 cm x 5 cm; area = 25 cm ²
Cathode	Gold plated aluminum: 5 cm x 15 cm; area = 75 cm ²
Anode and cathode compartments	5 cm x 15 cm x 0.2 cm; volume = 15 mL.
Cation exchange membrane	Du Pont Nafion Perfluorinated Membrane Series 300: Nos. 324 and 350; resistivity = 4.5 and 3.7 ohm·cm ²
Flow rates (typical)	Anolyte: 9.2 mL/s (9.2 cm/s) Catholyte: 7.9 mL/s (7.9 cm/s)
Electrical	Anode current densities: Up to 5000 A/m ² . Applied voltage: Up to 115 V.

For some of the experiments a titanium and a platinum electrode was used as an anode. In these tests, a sheet of the metal was attached to the aluminum plate using epoxy and the exposed portion of the original anode was sealed with an insulating material.

The flow scheme is shown in Figure 4. The anolyte and catholyte tanks were 10 L plastic bottles, which at the start of the run were filled with 7.7 L of saturated sodium bicarbonate (anolyte) and 1.5 L of one percent potassium hydroxide (catholyte). Distilled water and chemically pure reagents were used to make up the solutions. The potassium hydroxide was used to provide conductivity to the catholyte at the start of each run. The catholyte tank was purged with nitrogen to prevent absorption of carbon dioxide from the atmosphere. This nitrogen purge also served to vent the small amount of hydrogen that was evolved at the cathode (Equation 4).

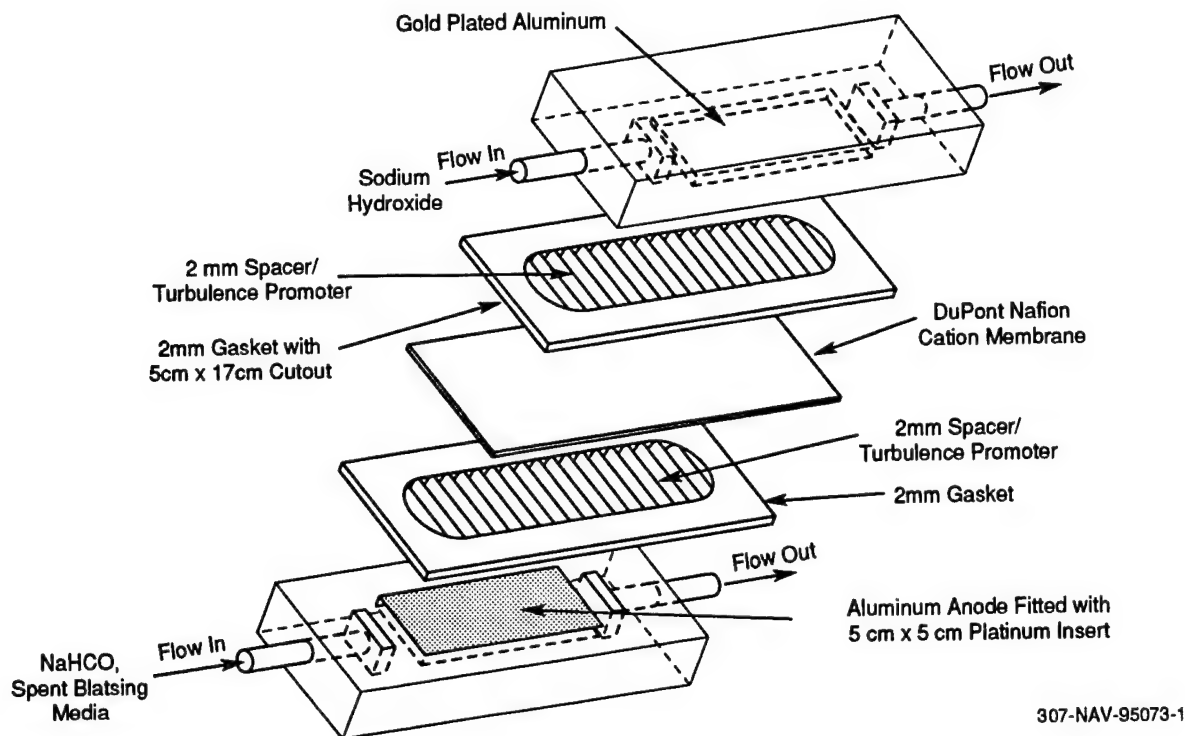


Figure 3. Detail of the Electrochemical Cell Used in the Tests

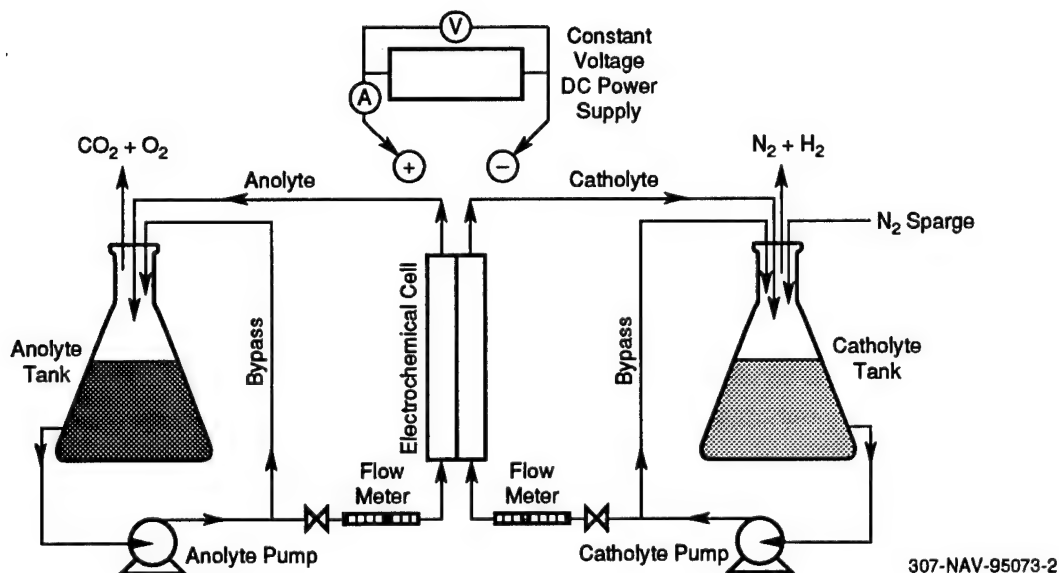


Figure 4. Schematic of the Experimental Flow System

Most of the runs were done with flow rates of 9.2 mL/s (anolyte) and 7.9 mL/s (catholyte), but a few tests were done at different flow rates to determine the effect of electrolyte velocity on the current-voltage characteristics of the cell. The solutions were circulated with peristaltic pumps through calibrated rotameters. Samples of electrolyte were withdrawn at regular intervals and analyzed for sodium content. Runs lasted for a few hours to several days (with overnight breaks).

Corrosion of the gold plated aluminum occurred in some of the runs and resulted in membrane fouling with attendant increased voltages and diminishing currents. Inspection of the electrolyte and membrane revealed a white particulate precipitate in the solution and on the membrane surface. Soaking the membrane in acid overnight generally did not restore the membrane to its original condition, so fresh membranes were used for most runs. It is believed that this condition arose mainly as a result of using an aluminum cell, and would not occur with a plastic cell and platinum/titanium anodes.

4. RESULTS AND DISCUSSION

A summary of the experiments completed is given in Table 3 and the data obtained during these runs are given in the Appendix.

Table 3. Summary of Experiments

Exp No.	Electrode		Resistance* R _{eff} (ohms)	Remarks
	Anode	Cathode		
P1	Gold	Gold	-	Determine current-voltage characteristics
P2	Gold	Gold	-	
P3	Gold	Gold	-	Determine velocity dependence
E1	Gold	Gold	1.3	Anode corrosion in evidence
E2	Aluminum	Gold	37.7	Current decreased rapidly
E3	Titanium	Gold	5.8	New membrane. High voltage, poor currents due to passivation.
E4	Platinum	Gold	1.1	New membrane, high efficiency
E5	Platinum	Gold	2.0	New membrane, extended run
* Effective resistance estimated from R _{eff} = Mean voltage/mean current				

Before presenting results on the effectiveness of the sodium separation, the current-voltage characteristics of the cell are first described.

4.1 Current-Voltage Characteristics

The current-voltage plots shown in Figure 5 for the preliminary experimental runs indicate that on increasing the voltage there is initially little increase in the current until some critical voltage, known as the thermodynamic decomposition voltage, is reached. It is the sum of the reversible or thermodynamic equilibrium potentials at the anode and cathode that are associated with the electrode reactions. These thermodynamic potentials, E, are obtained from the standard electrode potentials for the electrode reactions, E⁰, and corrected for the actual electrolyte concentrations using the Nernst equation:

$$E = E^{\circ} + (RT/nF)[\ln (\prod c_i^{\nu_i})_{\text{oxidized species}}]/[\ln (\prod c_i^{\nu_i})_{\text{reduced species}}] \quad (6)$$

where the c_i are the concentrations (actually activities) of the reacting species, the ν_i are their stoichiometric coefficients in the electrochemical equation, n is the number of electrons transferred, R is the gas constant, T the absolute temperature, and F the Faraday constant. The group RT/F is the characteristic potential, sometimes called the Nernst potential, and has a value of 25.7 mV at 25 °C.

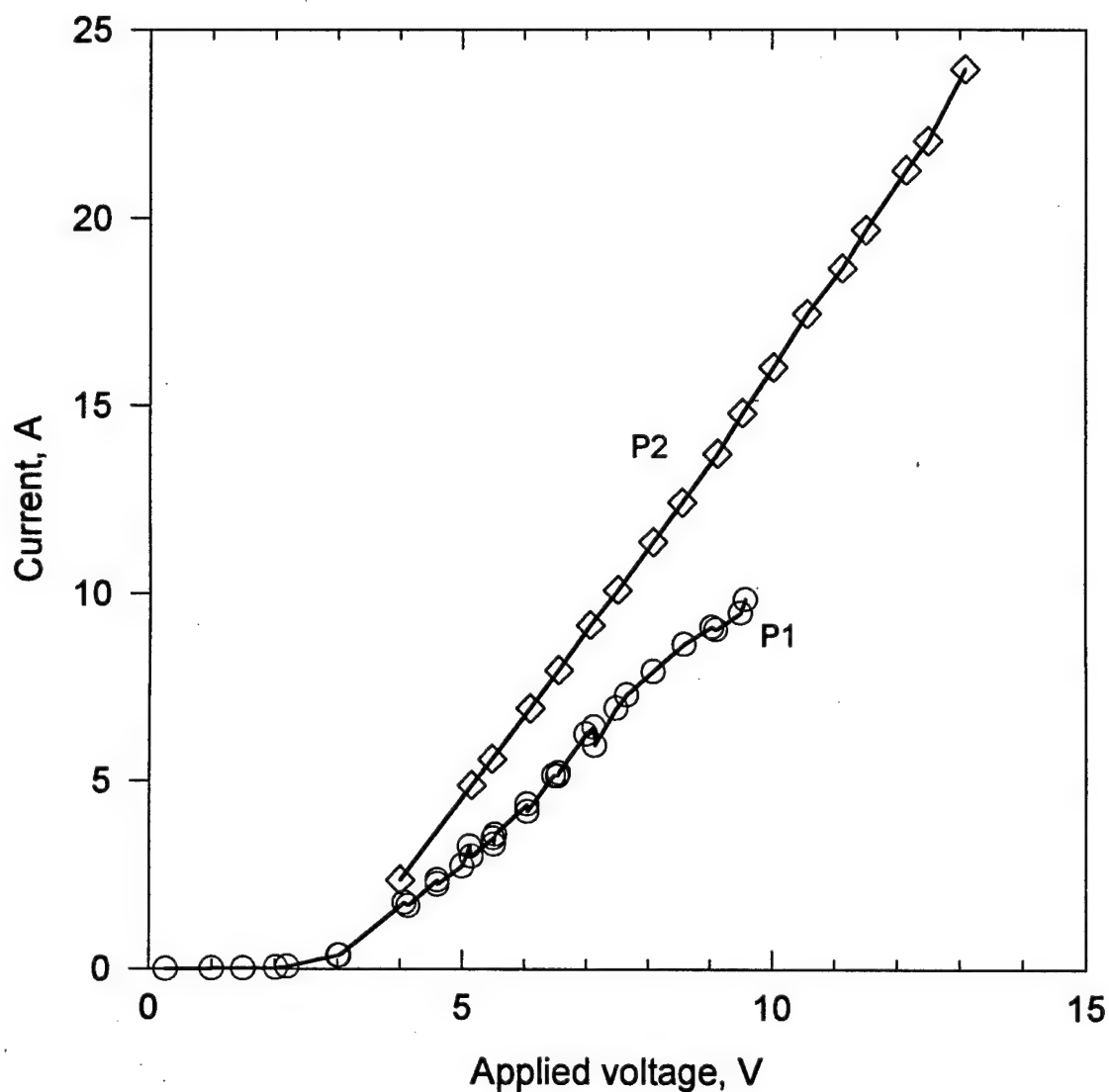
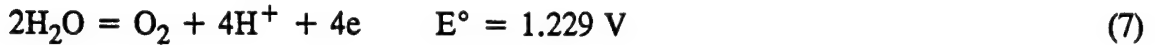


Figure 5. Current Voltage Characteristic for the Cell.
Gold plated electrodes. Anolyte: 9 percent NaHCO_3 ;
Catholyte: 1 percent KOH ; Flow Rate: 7.25 mL/s.

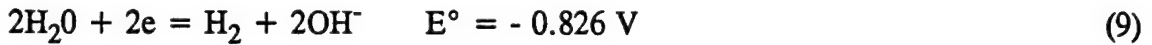
For example, at the anode, the electrode reaction is:



so, with $n = 2$, the electrode potential at the anode becomes:

$$E_a = 1.229 - 0.059 \text{ pH} + 0.015 \log p_{\text{O}_2} \quad (8)$$

Here we have use the definition $\text{pH} = -\log \text{H}^+$. The pH of the anolyte is around 8 and assuming the oxygen is at a pressure of 1 atmosphere, the reversible anode potential is found to be 0.76 V. Similarly, for the cathode:



so Equation (8) becomes

$$E_c = -0.059 \text{ pH} - 0.029 \log p_{\text{H}_2} \quad (10)$$

Here we have used $\text{pH} + \text{pOH} = 14$. The pH of the catholyte is around 14 and assuming the hydrogen is at a partial pressure of 1 atmosphere, the reversible cathode potential is found to be -0.826 V. The thermodynamic decomposition voltage for the cell, E_d is then:

$$E_d = E_a - E_c = 0.76 - (-0.826) \approx 1.6 \text{ V} \quad (11)$$

In addition to the thermodynamic decomposition voltage, the applied voltage must overcome the electrode overpotentials to achieve a finite current. Overpotentials for hydrogen evolution at the cathode and oxygen evolution at the anode depend on the electrode material and on the current density. At low currents on gold electrodes, the hydrogen overpotential is about 0.3 V and the oxygen overpotential is about 0.7 V for a total overpotential of 1 V. Adding the overpotential to the electrode potentials results in a minimum applied voltage for current onset of about 2.6 V, which falls in the 2 to 3 V range observed experimentally.

To increase the current further, the applied voltage must overcome the voltage drop due to the electrical resistance of the electrolytes and the membrane. This "cell resistance" can be estimated from the slope of the current-voltage curve. It is seen from Figure 5 that although both runs P1 and P2 had essentially the same minimum voltage for current onset, the current increased more rapidly in the case of Run P2. The greater slope indicates a lower cell resistance. The lower resistance could result from more concentrated electrolyte solutions or from a higher velocity of the electrolyte through the cells. The higher velocity thins the boundary layer so decreasing concentration polarization effects. Based on the slopes of these current voltage plots, the resistivity of the cell decreased from 1.4 ohm·m for Run P1 to 0.8 ohm·m for Run P2.

Because the cell potential directly determines the power consumption, it is important to keep it as low as possible. One method of reducing the concentration overpotential is to agitate or stir the electrolyte solution near the electrode, which serves to increase mass transfer rates through the boundary layer, and also scours gas bubbles from the electrode surface. In flow cells, this effect is achieved by increasing the electrolyte flow rate. In our tests, increasing the electrolyte flow rate from 7.25 to 18 cm/s decreased the cell resistance from 1.4 to 0.74 ohms as shown in Figure 6. Operation at the high end of this range would reduce the cell power consumption by some 50 percent. Commercial cells operate at velocities up to 60 cm/s.

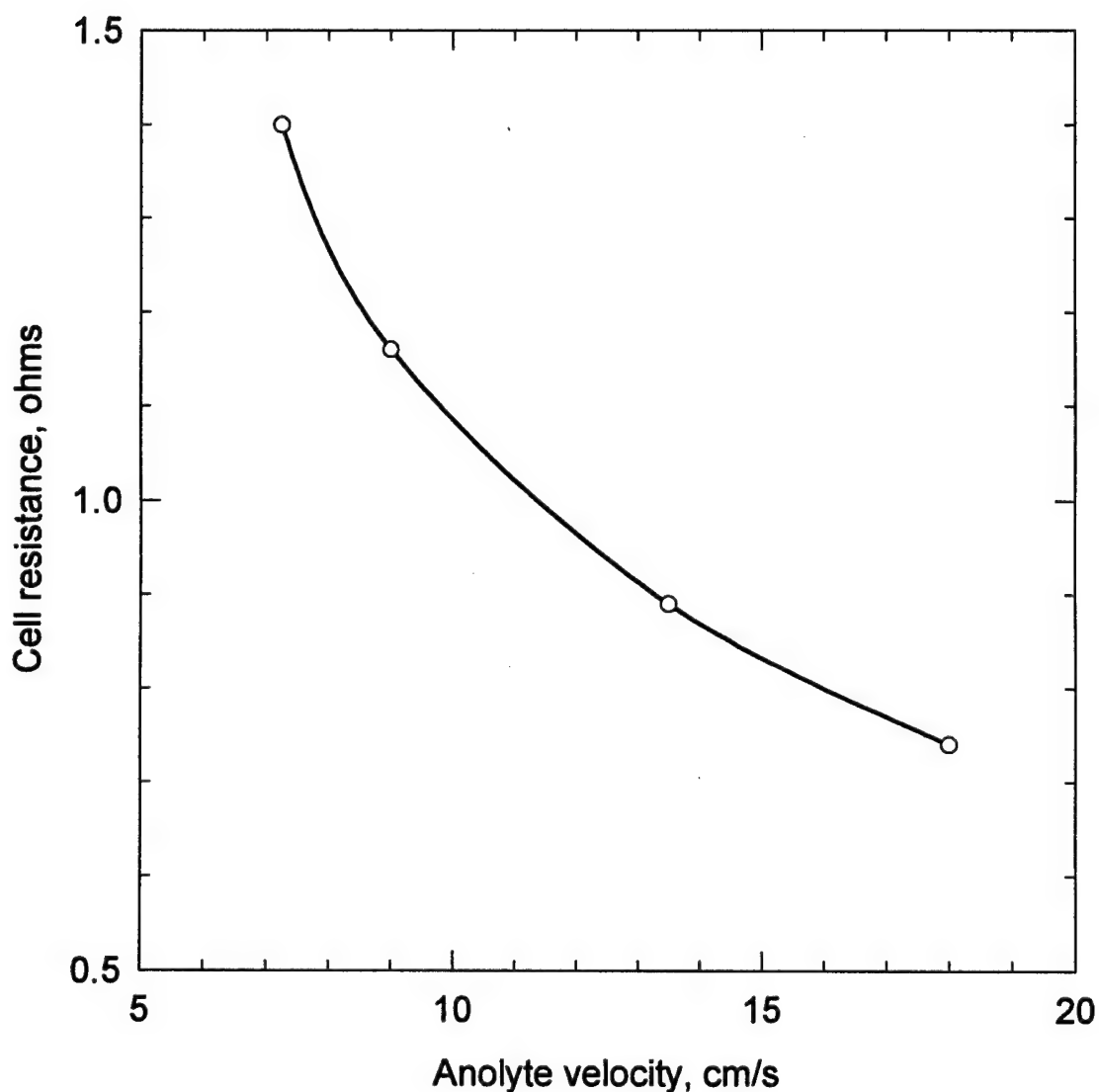


Figure 6. Effect of Electrolyte Velocity on Cell Resistance

It is noted that increasing the conductivity of the electrolyte will also reduce the cell resistance. The conductivity can be increased by increasing the concentration and temperature of the electrolyte. In our case, the concentration of the anolyte is determined by the desired final concentration of the depleted bicarbonate effluent. The lower this value, the lower the conductivity of the anolyte, and the greater the IR drop across the cell. Clearly, the concentration must be set at the highest level that is still acceptable for recycling or discharging this effluent stream.

Increasing the temperature offers an attractive means of increasing the conductivity of the electrolyte. Sufficient hydrogen is produced electrochemically to raise the temperature of the incoming water by about 30 °C. It has been reported that a 30 °C temperature increase can reduce the applied voltage from 14 to 9 volts (7), with a corresponding savings in electrical energy of 35 percent.

4.2 Sodium Separation

Of the five runs completed (E1 to E5), only those with a platinum anode (Runs E4 and E5) provided meaningful data. During the preliminary tests the gold anode showed some signs of corrosion, and at the high current densities used in the actual runs, corrosion rates became unacceptable and it was decided to try alternative anode materials. Aluminum, titanium, and platinum anodes were tried. Both the aluminum and the titanium electrodes passivated, requiring very high voltages to drive a current. It is noted that although titanium anodes are widely used in electrochemical processing (7, 10), these electrodes typically have precious metal oxides or other electroactive coatings.

The results obtained with the platinum electrode are shown in Figure 7 as a plot of the sodium concentration in the catholyte against the amount of electricity passed. Although there is some scatter in the data, runs E4 and E5 show fairly consistent, reproducible results, indicating an ongoing transfer of sodium with current passed. To gauge the efficiency of the electrochemical sodium separation process, two parameters are considered, namely the current efficiency and the energy consumption.

4.3 Current Efficiency

Based on the slopes of the plots in Figure 7, some 1.6 amp-hour (Ah) of electricity are required per gram of sodium transported across the membrane. According to Faraday's law, 96,500 coulombs (C) are required to transport each mole (23 grams) of sodium across the membrane. This is equivalent to about 1.2 Ah/g sodium. Defining the current efficiency as the ratio of the current theoretically required to the current actually passed results in a current efficiency of 1.2/1.6 or 75 percent. It is noted that in some runs, an increase in the volume of catholyte was observed, so actual current efficiencies might be better than calculated here.

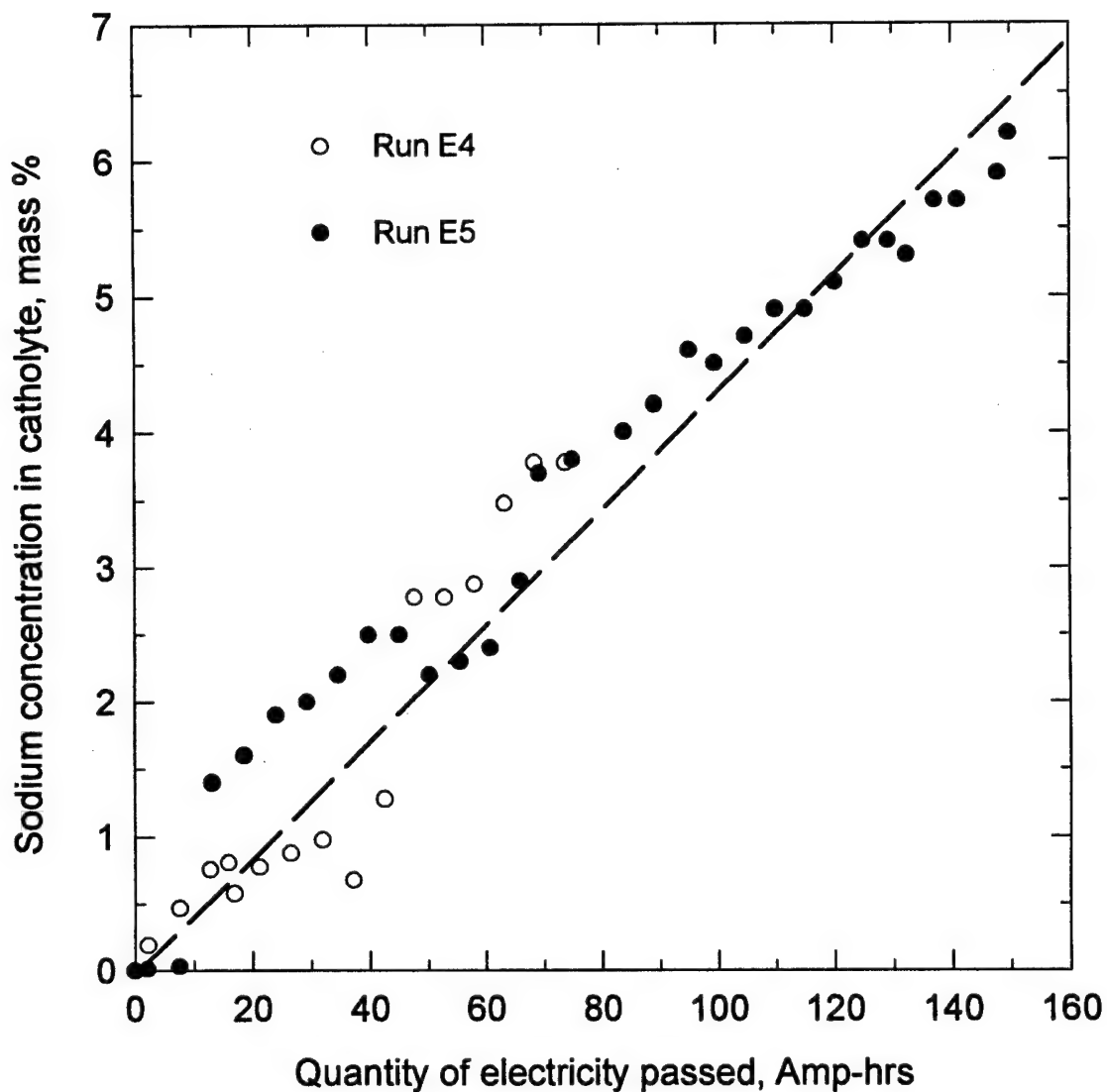


Figure 7. Increase in the Catholyte Concentration with the Quantity of Electricity Passed

Values of the current efficiency below 100 percent are usually attributed to leakage currents and transport of species other than sodium. Leakage currents arise from current paths through the manifolds of multicompartiment cells. They are expected to be negligible in the experimental equipment used here as there was only a single anolyte and catholyte compartment, and the feed solutions were electrically isolated. Means for minimizing leakage currents are usually included in commercial systems.

The cation exchange membrane is impermeable to carbonate ions and hydroxyl ions, so these species cannot contribute to the loss in current efficiency. The only cation other than sodium that is present in sufficient quantity to affect the current efficiency is hydrogen. As discussed, one mole of hydrogen is formed at the anode for each mole of sodium transported across the membrane. However, the kinetics of the reaction between the hydrogen ions and the bicarbonate ions is very rapid, and it is unlikely that any hydrogen ions will be transported before being converted back to water:



Based on these arguments and the high value of the current efficiency obtained experimentally, it is concluded that competing transport processes are not likely to be a problem in a commercial-scale cell.

4.4 Energy Consumption

The actual energy consumed is given by the product of the applied voltage, the current and the time taken to transport a given quantity of sodium. It may be obtained from the area under a plot of the quantity of electricity passed against applied voltage as shown in Figure 8. These data give energy consumption rates of 15 kWh/kg for Run E4 and 50 kWh/kg for Run E5 and are some 2 to 7 times the consumption rates reported for a pilot-scale electrochemical sodium recovery system (see Table 4). This difference is due mainly to the higher voltages (10 to 20 V) that were used experimentally. In fact, increasing the electrolyte flow rate would have reduced the power consumption for Run E4 to about the same as that reported previously (7), namely 7 kWh/kg sodium (about 1 kWh/lb sodium bicarbonate). The reason for the very high voltages obtained in Run E5 is not known, but may be due to poor electrical contact between the platinum anode and the support plate.

We can estimate a theoretical minimum energy requirement using:

$$\epsilon = F (E_a - E_c) \text{ J/mol} \quad (13)$$

where F is Faraday's constant ($= 96,500 \text{ C}$) and E_a and E_c are the thermodynamic or reversible potentials needed to drive the electrode reactions at the anode and cathode respectively. As discussed previously, the thermodynamic potential is approximately 1.6 V so the theoretical energy ϵ is 154 kJ/mol or about 2 kWh/kg of sodium transferred across the membrane. Note that because the electrode reactions do not involve the discharge of sodium ions, the theoretical energy is independent of the concentration of sodium ions in the electrolyte.

The energy consumed in the experiments ranged from 7 times (Run E4) to 25 times (Run E5) the theoretical minimum. The theoretical energy will be exceeded due to current inefficiencies as discussed above, but mainly because the applied voltage is higher than the thermodynamic value. Higher than theoretical voltages are needed to overcome the anodic

and cathodic overpotentials as well as the ohmic resistance of the electrolytes and of the membrane.

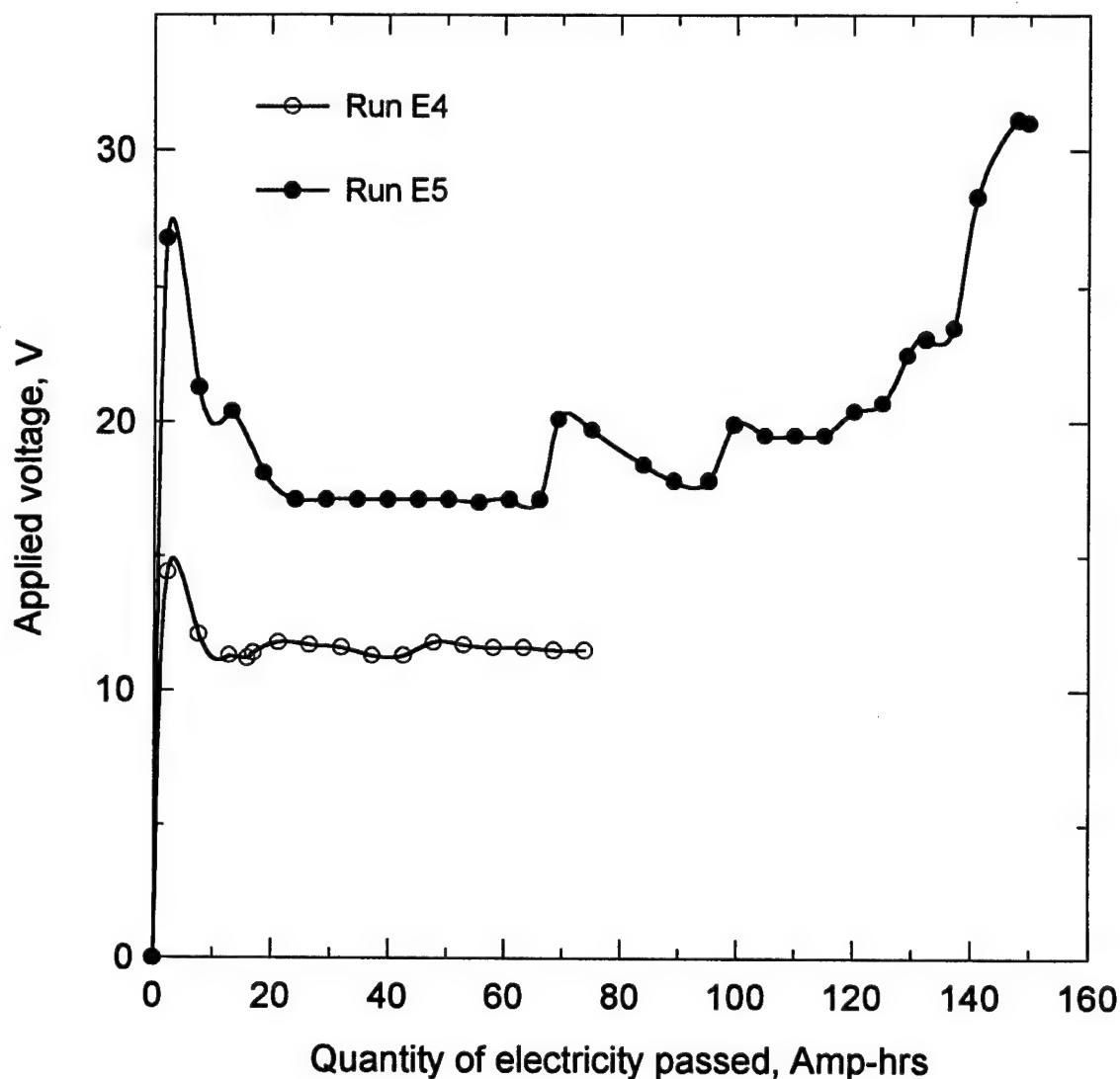


Figure 8. Variation of Applied Voltage with Quantity of Electricity Passed in Runs E4 and E5. Electrolyte velocity = 9 cm/s.

Commercial electrochemical cells in the chlor-alkali industry typically operate at an applied voltage of from 3 to 3.5 V over a cell thickness of about 4 mm (anode plus cathode compartments) and achieve current densities of up to 10 kA/m². Unlike chlor-alkali cells where the electrolyte concentrations can be kept high, in sodium concentration systems, the anolyte concentration is to be reduced from near saturation to below the local discharge limit for sodium. To compensate for the higher resistance of the anolyte, sodium recovery units are operated at higher voltages and lower current densities.

Table 4. Performance Characteristics of Electrochemical Cells

Parameter	Run E4 (This work)	Run E5 (This work)	Chlor- alkali (10)	Sodium Recovery (7)
Current efficiency, percent	75		-	80
Energy ^a ; kWh/kg sodium	14.9	49.9	5.4 ^b	6 to 7
kWh/lb sodium bicarbonate	1.9	6.2	0.7	0.7 to 0.9
Electrode spacing, mm	4	4	4	4 ^c
Applied voltage (mean), V	11.5	20.2	3.5	7
Voltage gradient, kV/m	2.88	5.05	0.88	1.75
Current density, kA/m ²	4	4	10.0	Up to 6.0
Cell resistivity ^d , ohm.m	0.72	1.26	0.09	0.29
^a Theoretical value is 2 kWh/kg sodium (0.25 kWh/lb sodium bicarbonate). ^b Based on data given for chlorine. ^c Assumed. ^d Calculated from the ratio of voltage gradient and current density.				

To compare the current-voltage characteristics of the various cells on a common basis, we have determined in Table 4 the cell resistivities for a typical chlor-alkali cell, the pilot-scale sodium recovery cell, and the experimental cell. As can be seen, the resistivity of the test cell is at least 8 times higher than for chlor-alkali systems and more than double that for the sodium recovery unit. Whereas a higher resistivity than a chlor-alkali system is expected in view of the lower electrolyte concentrations, the comparison with the sodium recovery unit indicates that the test cell should be run at higher electrolyte velocities to reduce energy consumption. Further insight into cell resistance can be had by determining the resistivity of the electrolyte solutions.

4.5 Electrolyte Resistivity

The resistivity ρ of the electrolyte can be estimated from the molar conductivity of ions in solution (11) and the voltage gradient is then obtained for the prevailing current using Ohms law:

$$\Delta V/L = \rho i \quad \text{V/m} \quad (14)$$

where L is the depth of the electrolyte compartment and i is the current density.

Calculated values of the electrolyte resistivities and the corresponding voltage drop are summarized in Table 5 for an anolyte concentration of 9 percent (near saturation) and a catholyte concentration of 2 percent, which are representative of the test conditions. In addition, the table includes values for the depleted anolyte, here taken to be 0.45 percent sodium bicarbonate (95 percent recovery), and a target catholyte concentration of 10 percent sodium hydroxide.

Table 5. Electrolyte Properties

Parameter	Sodium	Bicarbonate	Sodium	Hydroxide
Molar conductivity $\times 10^3$, $\text{m}^2/\text{ohm}/\text{mol}^*$	5.01	4.45	5.01	19.8
	Anolyte, NaHCO_3		Catholyte, NaOH	
	Saturated	Depleted [‡]	Test	Target
Concentration, mass percent mol/m^3	9 1070	0.45 54	2 500	10 2500
Resistivity, $\text{ohm}\cdot\text{m}$	0.10	1.95	0.08	0.016
Current density, kA/m^2	5	2	5	5
Voltage gradient [†] , kV/m	0.5	4.0	0.4	0.08
Voltage for 2 mm cell thickness, V	1.0	8.0	0.8	0.2
* From (11). ‡ Assuming a 95 percent sodium recovery. † From Equation (14).				

According to the calculated values in Table 5, the voltage drop over the electrolyte solutions during the test was at most about 2 V. The sum of the reversible potential (1.6 V), the hydrogen and oxygen overpotentials (2.3 V at $5 \text{ kA}/\text{m}^2$), the ohmic drop across the electrolyte (2 V) and the voltage drop across the membrane (about 0.25 V) comes to 6.2 V. The applied voltage in run E4 was about 5 V higher, and in Run E5 at least 14 V higher, than this estimated voltage. The difference may be due in part to concentration polarization (boundary layer effects). However, the operating conditions were essentially the same in the two runs in spite of the very different voltages, so the excess voltage drop appears to be due to poor electrical contact or membrane fouling.

4.6 Membrane Characteristics and Fouling

Several times during the test series, it was found that excessively high voltages were required to maintain the desired current density. In some cases, the current decreased to near zero even on increasing the applied voltage to 60 V. The fouling seemed to occur rapidly after operating for some time without any noticeable effect. It did not appear to be related to increased concentrations of NaOH in the catholyte.

Inspection of the membrane revealed a white precipitate that was probably a metal hydroxide or carbonate. The source of the precipitate was not determined, but might have resulted from corrosion of the aluminum cell. A calcium carbonate precipitate is unlikely in that there was virtually no calcium in the sodium hydroxide used, and the electrolyte solutions were prepared from distilled water.

Rinsing the membrane in water and even soaking it in dilute hydrochloric acid overnight did not restore the current although visible evidence of the precipitate was removed. It is noted for example that the sudden increase in voltage in Run E5 at 70 amp-hrs occurred after an overnight break which included conditioning the membrane in acid. At 120 amp-hrs (coinciding with a second overnight break), after about 12 hours of operation, the current declined rapidly toward zero in spite of increasing the applied voltage by 50 percent. A decrease in performance was not observed in Run E4, which was completed after 7 hours of operation without any breaks.

On replacing the membrane, current densities were restored to their original values. It seems clear that the high applied voltages were a result of membrane degradation. The membrane manufacturer has stated that in addition to metal hydroxides, hardness elements and silica in the water might be responsible for the fouling (12). Sequestrants can be added to keep these compounds in solution. We believe however that the fouling is related to the corrosion of the metal test cell used and will not present a problem in cells in which PVC or similar plastic will be used as a material of construction. This contention is supported by results reported for tests with a PVC pilot plant using the identical membrane and similar feed solutions in which membrane fouling did not occur (7).

4.7 Sodium Hydroxide Concentration

To reduce the overall operating costs, it is important that the concentration of sodium hydroxide in the catholyte be as high as possible. The membranes used in the tests (Nafion series 300) have reported capabilities of attaining a concentration of 16 to 20 percent NaOH. In our tests we achieved concentrations of above 6 percent without any decrease in current efficiency (see Figure 7). Although higher concentrations were not reached in the Phase I investigation due to the unrelated problem of membrane fouling, there is no reason to believe that a concentration of 15 percent cannot be achieved. It is noted that other membranes in the Nafion series (series 900) are available for production of sodium hydroxide concentrations of up to 35 percent. If required, the sodium hydroxide can be further

concentrated by thermal evaporation.

5. ECONOMIC ANALYSIS

The use of sodium bicarbonate blast media for paint stripping and degreasing meets one of the prime objectives of the Department of Defense's pollution prevention initiatives, namely, the substitution of a process that uses environmentally benign chemicals for one that uses toxic organic solvents and/or hazardous chemicals. However, the process produces large quantities of waste streams containing toxic and hazardous materials, such as heavy metals and oils and greases.

Electrochemical concentration and purification of spent sodium bicarbonate blasting media reduces the volume of toxic waste requiring disposal and at the same time reduces process costs by recovering the blasting medium and substantially reducing the cost of waste disposal. In this section, the costs of recovering the spent sodium bicarbonate blasting media by electrochemical means and disposing of any effluents will be compared to the present method of treatment.

The plant design is based on the ACCUSTRIPTM blasting process at a NASA facility responsible for the maintenance and repair of a fleet of 37 aircraft (2). The facility operates 250 days per year, consumes 25 lb/day of bicarbonate blast media, and produces several waste streams as shown in Figure 9. Because the concentrations of certain heavy metals exceed local discharge limits, the solid and liquid wastes from the blasting vats as well as the floor wash are considered toxic and have to be disposed of off-site as hazardous wastes. In the NASA facility, the metal concentrations in the rotoclone effluent however do not exceed specifications and are disposed of to a municipal drain as a non-hazardous waste.

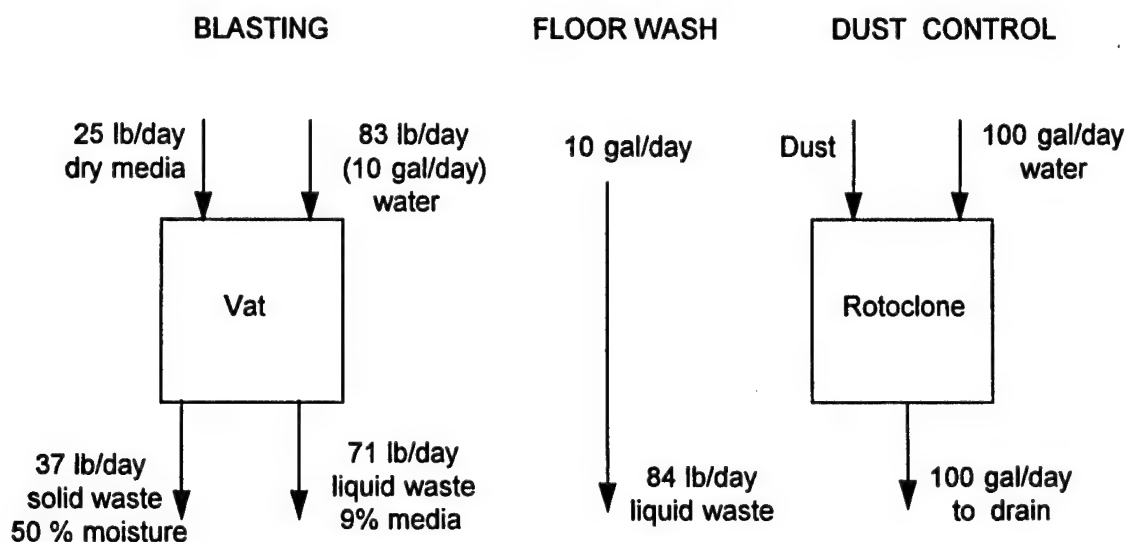
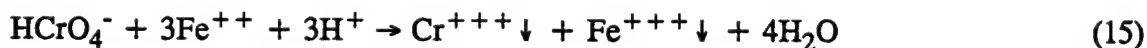


Figure 9. Waste Streams Generated in the ACCUSTRIPTM Blasting Process

5.1 Conceptual Design

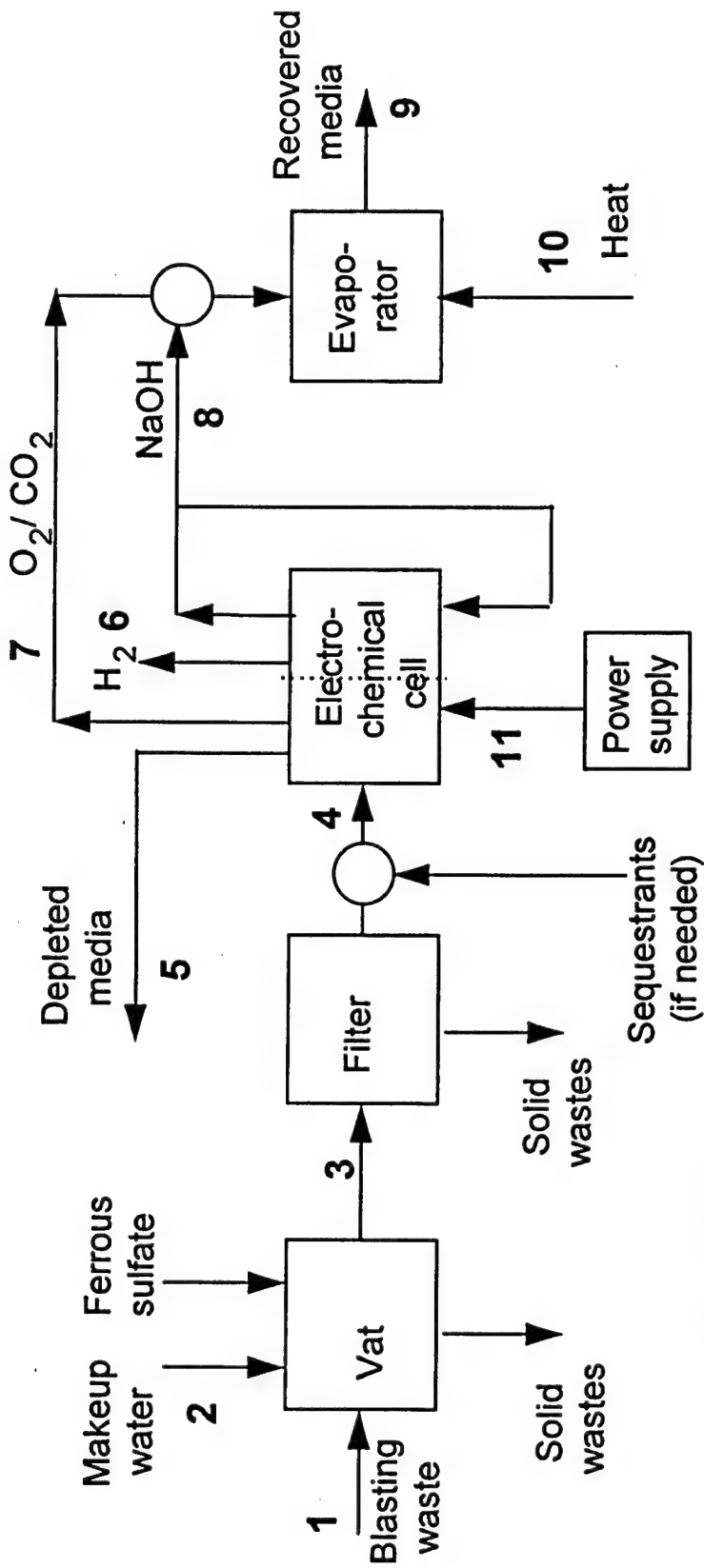
In the treatment/recovery scheme proposed here, the solid and liquid hazardous wastes will be combined and sufficient water added to dissolve all the spent blast media. This water will come from the floor wash of 10 gal/day (37.9 L/day) plus a small portion of about 13 gal/day (49.2 L/day) of water from the rotoclone system, and will be added to the wastes in the vat to produce a combined liquid waste of some 33 gal/day (124.9 L/day = 124.9 kg/day = 275.3 lbs/day). This will be the feed stream to the treatment train. The plant is designed to produce an intermediate product of 15 percent sodium hydroxide, which will be converted back to sodium bicarbonate by reaction with the carbon dioxide evolved in the electrochemical cell.

In addition to being nearly saturated with sodium bicarbonate, the feed stream is expected to contain oil and grease, suspended solids, and dissolved heavy metals. The heavy metals of main concern are chromium, lead, and zinc (2). However, as was shown in Figure 1, at the high pH and high bicarbonate concentration, lead and zinc will be well below their local discharge limits of 1.5 and 6 mg/L respectively. It is proposed to remove the chromium by reducing it from the hexavalent form to the insoluble trivalent form with ferrous sulfate coagulant (5, 13):



The ferrous iron is itself oxidized to the ferric form and precipitates as the hydroxide or carbonate. Part of the precipitates will be removed by settling and the remainder removed in a cartridge filter. Although the levels of oil and grease do not exceed the discharge limit of 200 mg/L [2], they should be removed to avoid contamination of the electrodes and membrane in the electrochemical concentrator. It is expected that the oil and grease will be coagulated by the ferrous sulfate and be removed along with the suspended solids and precipitates in the cartridge filter. If not, a special purpose oil removal system, for example an oleophilic belt skimmer, will be added to the treatment train.

A simplified flow sheet for the treatment process, together with the flow rates for the major streams, is shown in Figure 10. The solid wastes discharged from the vat and the filter shown in Figure 10 are just the suspended solids and heavy metal precipitates (see Table 1). Table 6 compares the solid and liquid wastes generated for the cases of untreated and treated (electrochemical) spent blast media. All of the wastes generated in the untreated case are considered to be hazardous including the liquid wastes. Only the solid wastes associated with oil and grease coagulation and heavy metal precipitation for the treated case are considered to be hazardous. *These wastes have been estimated (see Table 6) to be less than 40 lbs/yr or less than 0.1 bbl/yr. Table 6 shows that the quantity of solid hazardous wastes have been reduced by over 99 percent and liquid hazardous wastes have been eliminated altogether.* For electrochemical treatment, the depleted blast media can be discharged directly to drain because all of the hazardous contaminants have been removed.



Stream No.	1	2	3	4	5	6	7	8	9	10	11
Component	Blast waste	Makeup water	Feed	Filtrate	Depleted media	H ₂	O ₂ /CO ₂	NaOH	Recov'd media	Fuel oil	d.c. power
NaHCO ₃	25.00		25.00	25.00	1.25				23.75		
NaOH								11.31			
Water	166.60	111.18	277.78	277.78	280.32		2.26	64.09			
H ₂ or O ₂						0.28	12.44				
CO ₂							14.70				
TOTAL	191.60	111.18	302.78	302.78	281.57	0.28	14.70	75.40	23.75		
Energy, 1000 Btu										64.09	
Energy, kWh										25.00	

Figure 10. Simplified Block Flow Diagram for the Electrochemical Treatment Process

Table 6. Wastes Generated for Treatment and Nontreatment of Spent Blast Media

Treatment of Spent Blast Media	Dry Solid Wastes (lbs/yr)	Liquid Wastes (gal/yr)	Comments
Untreated	4625†	5000†(a)	(a) Blasting liquid: 2500 gal/yr; floor cleaning: 2500 gal/yr
Treated	31.8†	-	Solid contaminants from liquid and solid wastes (Table 1)‡
	312.5	8400	Depleted blast media (Stream 5, Fig. 10); disposal to drain
Treated†/Untreated† (percent)	0.7	0	
† Disposed of as a hazardous waste ‡ Multiplied by a factor of 3 for sludge, etc.			

If needed, sequestrants can be added just upstream of the electrochemical concentrator to control hardness elements (calcium and magnesium scaling). Provided they are of the non-toxic variety, the presence of the small quantities of sequestrant and coagulant will not render the depleted blast media stream hazardous. The sodium content of this stream, about 1,000 mg/L, is not considered excessive, so it can be discharged to drain.

About 8 gallons of 15 percent sodium hydroxide solution are produced each day. As discussed, it is anticipated that the concentration of this intermediate product can be increased to more than 30 percent, if desired. Conversion back to sodium bicarbonate will involve reacting with the carbon dioxide evolved in the cell (Equation 2) and evaporation of the water. This recarbonation process has not been studied in detail, but may require a recrystallization step to obtain the recovered blast media in the desired particle size range. Additional carbon dioxide may also be required to make up for losses. An alternative would be to market the sodium hydroxide as a byproduct and use the proceeds toward the cost of makeup bicarbonate blast media. Currently, prices for sodium hydroxide are depressed at about 12¢/lb (50 percent solution) making this option unattractive economically. It may however be logistically attractive if there is a local need for caustic soda in that it simplifies the treatment plant.

5.2 Operating Costs

Major operating costs for the electrochemical treatment are summarized in Table 7. Electrical energy costs are based on the projected energy consumption of 1 kWh/lb sodium bicarbonate treated, or about 25 kWh per day. At a cost of 10¢/kWh, the electrical cost is 10¢/lb sodium bicarbonate treated. Evaporating the recovered sodium bicarbonate solution to dryness could add another 2¢/lb to the energy cost. However, the conversion of the sodium hydroxide to the final bicarbonate blast media product has not been evaluated in detail and may entail additional costs. The hazardous waste disposal costs are based on \$1000/bbl for solid wastes and \$2/gal for liquid wastes.

Without treatment, the primary operating cost is the cost of hazardous waste disposal. The cost of blast media makeup is approximately 20 percent of the cost of waste disposal. With electrochemical treatment, the primary operating cost is the electrical energy cost, closely followed by the cost of blast media makeup. The cost of energy for evaporation to a final product is about 25 percent of the electrical energy cost.

As shown in Table 7, the operating costs for the electrochemical treatment process are about \$1300 per year as compared to the \$22,600 needed for disposing the wastes if they are not treated. On accounting for the costs of blast media replacement, the proposed electrochemical treatment process has a potential savings of about \$25,600/yr. These savings must be used to pay for the capital equipment and its maintenance, and any costs that might be incurred.

Table 7. Estimated Differential Annual Operating Costs (\$/yr)

Item	Without Treatment (2)	With Treatment	Remarks
Blast media (a)	4250	425 (b)	(a) At \$0.68/lb (2). (b) Assuming 10 percent makeup.
Electric (c)	0	625	(c) At \$10¢/kWh and 1 kWh/lb sodium bicarbonate treated.
Gas or fuel oil	-	160 (d)	(d) Evaporation energy at \$10/10 ⁶ Btu.
Waste disposal†(e)	22600	90	(e) Excluding costs of disposing nonhazardous wastes.
Total	26850	1300	Potential savings of \$25,550/yr.
† Based on disposal costs of \$1000/bbl for solid wastes and \$2/gal for liquid wastes.			

5.3 Maintenance

The cell is similar to those used routinely in the chlor-alkali industry, but with the chloride-chlorine couple replaced with the more benign carbonate-carbon dioxide system. In addition, the anolyte in the chlorine cells is acidic, whereas in the bicarbonate system the anolyte will have a pH of neutral to moderately alkaline. It is therefore expected that the bicarbonate cell should perform as well as the chlor-alkali cells, where material degradation is reportedly not a major cost factor (14). In the present case, membrane fouling may well prove to a problem and more frequent membrane replacement or more stringent pretreatment may be needed. For purposes of this preliminary cost estimate, maintenance costs have been taken to be 5 percent of the capital cost (14).

5.4 Capital Equipment

To treat 25 lb/day of sodium bicarbonate at a current efficiency of 75 percent, the electrochemical concentrator must be sized to pass about 4,600 Amp-hrs per day. Assuming 12 hours operation per day and a mean current density of $3,000 \text{ A/m}^2$, an electrode area of 0.13 m^2 (1.4 ft^2) is required. A commercially available, skid mounted system is available for this duty at a cost of \$9,600 (15). As shown in Figure 11, the system is of modular design and can be readily expanded to increase its capacity by adding additional electrode pairs, and is available as a skid-mounted system.

At the start of the run the current is expected to be about 650 A (5000 A/m^2) at 6 V, and toward the end could drop to about 260 A (2000 A/m^2) at 12 V. A power supply rated at 750 A, 12 V is suitable and will cost \$5,000 (15). The capital costs, which total \$19,400, are summarized in Table 8. These costs can be reduced substantially, or the capacity of the plant increased, by increasing the operating time from 12 to 24 hours per day.

5.5 Total Annual Costs - Base Case

The total annual costs for electrochemical concentration and purification are summarized in Table 9 and amount to \$2,270/year. This is some 90 percent less than the \$26,850/yr needed for fresh blast media makeup and waste disposal when the spent blast media is not treated. This represents a savings of \$24,580/yr and corresponds to a payback period of 9.5 months for the capital cost of the 25 lb/day spent blast media treatment train.

5.6 Effect of Plant Size and Disposal Costs on Total Annual Costs

The size of the plant for the base case is relatively small. Treatment plants for larger operations would benefit considerably from economy of scale, whereas economy of scale in waste disposal and blast media supply are independent of scale. Additional cost savings might be realized in the future as it is expected that the costs of waste disposal will continue to rise. For some U.S. Navy operations, the blast media rate can be as high as 150 lb/day (17) and the plant can be operating up to 24 hours per day. The costs of disposal can range

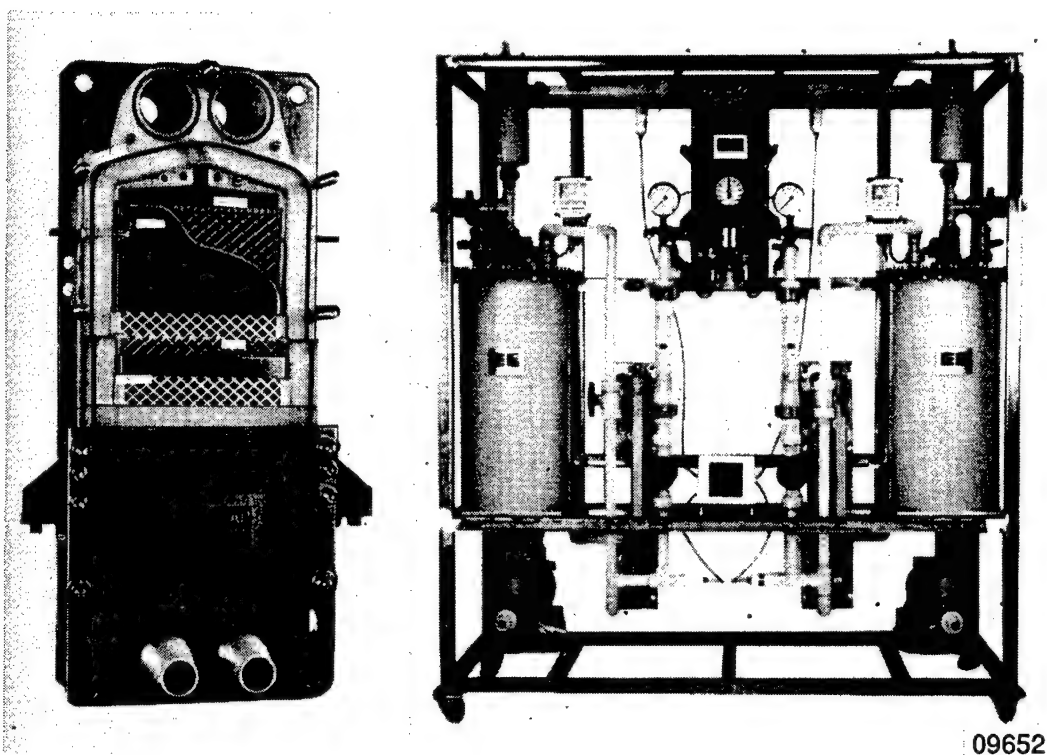


Figure 11. Detail of the Electrochemical Cell (Left) and the Skid-Mounted Cell with Pumps and Instrumentation (Right) (16)

Table 8. Capital Costs for the Electrochemical System†

Equipment	Description	Cost (\$)
Electrochemical cell	ElectroSyn Cell, ElectroCell AB, Sweden Electrode area: 0.16 m ² ; Number of electrode pairs: 4 Membrane: Du Pont Nafion 300 Series (4) Anode: Platinum on titanium (2) Cathode: Stainless steel (3)	9600
Power supply	Rapid Power Technologies. 750 amps, 0 - 12 volts. Air cooled.	5000
Miscellaneous	Tanks, stirrers, pumps, dosing pumps, filter, instruments and controllers (estimated at 50 percent of cell cost).	4800
Total		19400

† 12 hours operation per day.

Table 9. Annualized Costs of Electrochemical Processing (\$/yr)

Treatment	Item	Cost
Electrochemical, \$/yr	Operating costs (Table 7)	1300
	Maintenance†	970
	Total Annual Costs	2270
Untreated, \$/yr	Total (Table 7)	26850
Annual Savings, \$/yr		24580
Capital Cost, \$	(Table 8)	19400
Payback Period, yrs		0.8
, months		9.5
† Five percent of capital costs (Table 8)		

from \$1500/bbl for hazardous materials, down to as low as \$100/bbl for non-hazardous waste. The effect of the plant size, operating time and the unit disposal costs on the annual operating costs and the payback period will be estimated in this section:

- ***Plant size and plant operating time.*** The electrode area scales directly as the plant size and the capital cost of the electrochemical plant scales as the electrode area to a power less than one. Table 10 shows the electrode area required for an electrochemical plant size of 25 lb/day and 150 lb/day and operating times of 12 hr/day and 24 hrs/day. The capital cost of the plant is assumed to scale as the electrode area to the 0.7 power.
- ***Waste disposal costs.*** The solid waste disposal costs will be varied from \$100/bbl to \$1500/bbl, while the liquid waste disposal costs will be varied from \$0.20/gal to \$3.00/gal.

Tables 11 and 12 show the annual operating cost savings and payback period as a function of plant size, plant operating time, and unit waste disposal costs. In Table 11, the annual operating cost savings are estimated without including the maintenance costs (see Table 7). However, the payback period, as shown in Table 12, does include the maintenance costs.

Table 12 shows that, except for very low unit waste disposal costs, representative of non-hazardous waste disposal, and for the smallest treatment plant operating at 12 hrs/day, the period to payback the capital costs of the treatment train ranges from a little more than one year to about 3 months. After the payback period, electrochemical treatment of the

spent blast media will result in substantial savings in the annual operating costs (see Table 11) ranging from \$5,000 to \$37,000 for a blast media flow of 25 lb/day and from \$30,000 to \$220,000 for a flow of 150 lb/day; the lower savings corresponds to non-hazardous waste disposal and the higher savings corresponds to high unit waste disposal costs representative of hazardous waste disposal.

Table 10. Effect of Plant Size and Operating Time on Capital Cost of Treatment System

Plant size, lb/day	25		150	
Operating time, hr/day	12†	24	12	24
Electrode area, m ²	0.13‡	0.06	0.77	0.38
Capital cost, \$	19400	11942§	68000§	41869§
† Base case. ‡ See discussion in subsection 5.4. § Results scaled from base case. Scale factor = 0.7 power.				

Table 11. Savings in Annual Operating Costs (\$/yr)

Waste Disposal Costs		Blast Media Flow (lb/day)	
Liquid (\$/gal)	Solid (\$/bbl)	25	150
0.20	100	5290	31750
1.00	500	14300	85790
2.00	1000	25560	153330
3.00	1500	36810	220880
0.20	500	10300	61790
	1000	16560	99330
	1500	22810	136880

Table 12. Payback of Capital Costs (yrs)

Waste Disposal Costs		Blast Media Flow 25 lb/day		Blast Media Flow 150 lb/day	
Liquid (\$/gal)	Solid (\$/bbl)	12 hr/day	24 hr/day	12 hr/day	24 hr/day
0.20	100	4.5	2.5	2.4	1.4
1.00	500	1.5	0.9	0.8	0.5
2.00	1000	0.8	0.5	0.5	0.3
3.00	1500	0.5	0.3	0.3	0.2
0.20	500	2.1	1.2	1.2	0.7
	1000	1.2	0.7	0.7	0.4
	1500	0.9	0.5	0.5	0.3

It has been assumed that the automated electrochemical plant can be operated without additional labor costs. The labor associated with disposal of the hazardous wastes for untreated spent blast media will be offset by the labor associated with the operation of the electrochemical treatment train; less than 0.1 bbl/yr of hazardous waste are generated by the treatment train. Installation costs have also not been directly accounted for but should not be significant as the electrochemical components are supplied in a skid-mounted assembly.

6. CONCLUSIONS

A laboratory-scale investigation and feasibility study of the electrochemical conversion of sodium bicarbonate to sodium hydroxide has been completed.

The experimental investigation confirmed that sodium bicarbonate can be converted to sodium hydroxide in an electrochemical membrane cell. In these tests, the conversion was accomplished at a current efficiency of 75 percent and an energy input of 2 kWh per pound of sodium bicarbonate treated. At a cost of 10 ¢/kWh, the power cost amounts to 20 ¢/lb, about one-third the cost of sodium bicarbonate blast media at 68 ¢/lb. Based on the performance characteristics of the experimental cell and data reported in the literature, it appears that energy costs can be reduced to about 10 ¢/lb sodium bicarbonate treated by operating the cell at a higher electrolyte velocity than was used in the tests.

A waste treatment train based on the electrochemical process will essentially eliminate the need for off-site waste disposal, and recover 95 percent of the spent sodium bicarbonate blast media for reuse. A suitable electrochemical cell would contain platinum/titanium anodes, stainless steel cathodes, and be fitted with Nafion or similar cation membranes. Such cells are widely available commercially.

The electrochemical cell and power supply needed to treat some 25 lb/day of spent bicarbonate blast media will cost about \$14,600, and another \$4,800 is required for ancillary equipment to pretreat the waste stream. The cost of operating the electrochemical cell amounts to about \$2,220/yr, about 90 percent less than the \$26,850/yr needed for fresh blast media makeup and waste disposal, when the spent blast media is not treated. This represents a savings of \$24,500/yr and corresponds to a very short payback period of the capital costs of 9.5 months.

An economic analysis was also carried out for a larger plant size, a longer daily operation time, and varying unit costs of waste disposal. Except for very low unit waste disposal costs, representative of non-hazardous waste disposal, the period to payback the capital costs of the treatment train ranged from a little more than one year to about three months. After the payback period, electrochemical treatment of the spent blast media will result in substantial savings in the annual operating costs (see Table 11) ranging from \$5,000 to \$37,000 for a blast media flow of 25 lb/day and from \$30,000 to \$220,000 for a flow of 150 lb/day; the lower savings corresponds to non-hazardous waste disposal and the higher savings corresponds to high unit waste disposal costs representative of hazardous waste disposal.

The success of the electrochemical process depends on the ability to remove the heavy metal contaminants as well as the oil and grease from the spent blast media waste stream. The presence of these substances can lead to rapid membrane fouling and failure of the electrochemical system. Contaminant removal was not tested in the present study.

However, it appears that a reduction step to convert any hexavalent chromium present to the trivalent form, followed by cartridge filtration will be sufficient to remove the metals of concern (chromium, lead and zinc) which will precipitate out at the high pH of the bicarbonate solution.

The preliminary economic analysis indicates that electrochemical treatment is a cost effective means of eliminating the waste disposal problem associated with bicarbonate depainting. It is recommended that the long-term performance of the membranes be assessed using a commercial electrochemical cell running on spent blast media obtained from a depainting operation. In particular, the proposed pretreatment procedure for contaminant removal needs to be checked and refined if necessary. The data generated will allow a more detailed economic analysis, including the determination of the optimum concentrations of the depleted blast media and hydroxide streams, to be completed.

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APPENDIX. EXPERIMENTAL DATA

The raw data from the experimental runs are summarized below.

Run P1. Current-voltage characteristics

Gold Anode/Gold Cathode Membrane No. 1. Flow rate = 7.25 mL/s

Anolyte: 9 percent Sodium Bicarbonate Catholyte: 1 percent Potassium Hydroxide

Volts	Amps	Volts	Amps
0.27	0	4.07	1.76
0.10	0.01	4.60	2.36
2.2	0.06	5.15	3.00
3.03	0.36	5.51	3.31
4.13	1.68	6.03	2.69
4.6	2.25	6.48	5.16
5.00	2.74	7.13	6.45
5.50	3.48	7.49	6.94
6.05	4.2	8.09	7.99
5.12	3.27	8.59	8.65
5.53	3.58	9.01	9.12
6.05	4.39	9.58	9.87
6.54	5.15	6.03	3.54
7.14	5.97	6.56	5.24
Repeat		7.00	6.27
0.44	0	7.66	7.30
1.03	0	8.09	7.92
1.50	0.01	9.10	9.04
2.02	0.04	9.50	9.49
3.01	0.36		

Run P2. Current-voltage characteristics

Gold Anode/Gold Cathode Membrane No.1

Anolyte: 9 percent Sodium Bicarbonate Catholyte: 1 percent Potassium Hydroxide

Volts	Amps	Volts	Amps
4.00	2.37	9.13	13.75
5.15	4.90	9.53	14.84
5.48	5.60	10.03	16.06
6.10	6.95	10.57	17.48
6.55	7.95	11.13	18.69
7.07	9.17	11.51	19.72
7.52	10.12	12.15	21.29
8.09	11.41	12.50	22.04
8.56	12.46	13.09	23.95

Run P3. Velocity dependence

Gold Anode/Gold Cathode Membrane No. 1

Anolyte: 9 percent Sodium Bicarbonate Catholyte: 1 percent Potassium Hydroxide

Flow (mL/sec)	Volts	Amps	Resistance (calculated, ohms)
20	16.6	14.3	1.16
30	9.54	10	0.95
30	16.6	20	0.84
40	14.8	19.9	0.74

Run E1. Gold Anode/Gold Cathode
Anolyte: 9 percent Sodium Bicarbonate

Membrane No. 1
Catholyte: 1 percent Potassium Hydroxide

Time (hrs)	Volts	Amps	ppm Na
0.5	10.6	10.7	800
1.0	10.6	10.7	1100
1.5	10.6	10.7	1600
1.6	14.1	17.5	1200
1.8	14.1	18.0	1200
2.3	14.9	15.8	1900
2.4	10.5	10.5	1900
2.9	14.3	10.2	2200
3.4	20.2	10.4	2600
3.8	24.8	10.4	2900
4.0	25	8.9	2800

Sodium concentration in the anolyte initially 5000 ppm, ended at 2000 ppm. The gold plated anode was found to be very corroded at the end of the run.

Run E 2. Aluminum Anode/Gold Cathode
Anolyte: 7 percent Sodium Bicarbonate

Original Membrane No. 1
Catholyte: 1 percent Potassium Hydroxide

Time (hrs)	Volts	Amps	ppm Na
0.1	29.4	3.0	78
0.4	29.5	2.4	170
0.9	29.2	0.8	240
1.4	29.9	0.3	280
1.9	29.2	0.2	310
2.3	29.4	0.2	310

Sodium concentration in the anolyte initially 2300 ppm, ended at 2200 ppm.

Run E3. Titanium anode/Gold cathode
Anolyte: 9 percent Sodium Bicarbonate

Membrane No. 2
Catholyte: 1 percent Potassium Hydroxide

Time (hrs)	Volts	Amps	ppm Na
0.1	40.6	10.0	420
0.5	38.1	11.0	1900
1.1	35.4	9.4	4400
1.5	56.1	8.7	5900
2.1	58.5	8.5	7900
2.5	58.7	7.6	8000
3.0	58.9	7.2	9000

Sodium concentration in the anolyte initially 15,000 ppm, ended at 13,000 ppm.

Run E4. Platinum anode/Gold cathode
Anolyte: 9 percent Sodium Bicarbonate

Membrane No. 3
Catholyte: 1 percent Potassium Hydroxide

Time (hrs)	Volts	Amps	ppm Na
0.2	14.4	10.9	2100
0.7	12.1	10.8	4900
1.2	11.3	10.3	7800
1.5	11.2	10.3	8300
1.6	11.4	10.1	6000
2.0	11.8	10.6	8000
2.5	11.7	10.7	9000
3.0	11.6	10.9	10,000
3.5	11.3	10.6	7000
4.0	11.3	10.7	13,000
4.5	11.8	10.4	28,000
5.0	11.7	10.3	28,000
5.5	11.6	10.4	29,000
6.0	11.6	10.4	35,000
6.5	11.5	10.4	38,000
7.0	11.5	10.6	38,000

Sodium concentration in the anolyte initially 25,000 ppm, ended at 12,000 ppm.

Run E5. Platinum anode/Gold cathode
Anolyte: 9 percent Sodium Bicarbonate

Membrane No. 4
Catholyte: 1 percent potassium hydroxide

Time (hrs)	Volts	Amps	ppm Na
0.2	26.8	10.7	1100
0.7	21.3	10.8	1300
1.2	20.4	11.1	15,000
1.7	18.1	10.9	17,000
2.2	17.1	10.8	20,000
2.7	17.1	10.6	21,000
3.2	17.1	10.7	23,000
3.7	17.1	10.5	26,000
4.2	17.1	10.5	26,000
4.7	17.1	10.4	23,000
5.2	17.0	10.5	24,000
5.7	17.1	10.4	25,000
6.2	17.1	10.5	30,000
6.5	20.1	10.8	38,000
7.0	19.7	11.5	39,000
7.8	18.4	11.2	41,000
8.3	17.8	10.5	43,000
8.9	17.8	10.1	47,000
9.3	19.9	10.9	46,000
9.8	19.5	10.6	48,000
10.3	19.5	10.3	50,000
10.8	19.5	10.2	50,000
11.3	20.4	10.2	52,000
11.8	20.7	9.6	55,000
12.2	22.5	10.7	55,000

Time (hrs)	Volts	Amps	ppm Na
12.5	23.1	10.5	54,000
13.0	23.5	9.4	58,000
13.4	28.3	9.8	58,000
14.4	31.1	6.8	60,000
14.9	31.0	3.7	63,000

Sodium concentration in the anolyte initially 22,000 ppm, ended at 1,000 ppm. The gold plated anode was found to be very corroded at the end of the run.